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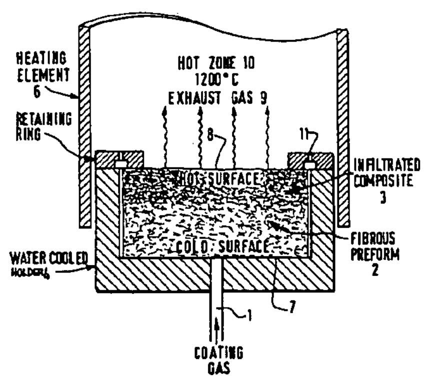
(54) Process for manufacturing fiber reinforced ceramic materials by chemical vapor infiltration.

(57) A process for manufacturing fiber reinforced ceramic material by chemical vapor infiltration by simultaneously providing a temperature gradient in the material and a combined pulsed pressure-temperature conditions in the CVD enclosure. A gas mixture comprising a nitrogen hydride and a gas selected from the group comprising silicon hydrides or silicon halides or a mixture thereof is injected in the enclosure for obtaining a silicon nitride deposition to fill up said material. The temperature gradient is provided by the use of a cold wall CVD enclosure along with an asymetrical heating of the material in said enclosure.



ORNL PROCESS

FIG.1
PRIOR ART

EP 0 499 004 A1

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION :

The invention relates to a process for manufacturing fiber reinforced ceramic materials by CVI (Chemical Vapor Infiltration) and particularly fiber reinforced ceramic material with silicon nitride matrix.

DESCRIPTION OF RELATED ART :

Ceramic fiber-ceramic matrix composites are known as having higher toughness and higher strengh as compared to conventional ceramics while retaining the properties of said ceramics such as refractoriness and high resistance to abrasion and corrosion.

Various processes based on chemical vapor infiltration have been already tested since the early 70's to form the matrix of fiber reinforced ceramic composites.

The matrices as well as the composite exhibited good mechanical properties, but the processing time takes several weeks which is unacceptable in an industrial process. Three different types of CVI processes were used for the manufacture of these composites : an isothermal process in which CVD gases diffuse into a preform, a thermal gradient process in which CVD gases are forced into the preform by a pressure gradient.

More recently, it has been proposed by D. STINTON et al in an article entitled "Synthesis of fiber-reinforced SiC compositeds by Chemical Vapor Infiltration" published in the Ceramic Bulletin, vol. 65, n°2 - 1986 -, a process of Chemical Vapor Infiltration providing for a thermal gradient and a pressure gradient step and illustrated on fig.1. In this process a fibrous preform 2 is retained within a graphite water-cooled holder 4 which cools the bottom 7 and side surfaces of the preform 2.

The top surface 8 of said preform 2 is exposed to the hot zone 10 created by the heating element 6 of the CVD enclosure, which creates a steep temperature gradient across the cooled portion of the preform, then across the hot portion where methylchlorosilane decomposes and Silicium Carbide SiC deposits on and around the preform fibers to form the matrix. As deposition of matrix material within the hot portion increases density and thermal conductivity of said preform, said hot portion progressively moves down.
The top surface becomes impermeable to gases, said gases flow radially through the preform to an annular void around the preform and exit through venting means 11. Depending on the type of material used as a preform (unidirectional, cloth or chopped fibers) SiC fibers/SiC matrix composite material is made in about 18 to 31 hours. However, even if the matrix diffuses from top to the bottom of the preform, the density of the composite thus obtained is at most 90 % and varies from about 50 % to about 90 %, which means that between 10 to 50 % of closed pores remain in the composite material.

It is also known from the article entitled "Pulse CVI of porous carbon" K. SUGIYAMA et al published in the journal of Materials Science Letters (6) - 1987 - pages 331-333. to use pressure pulse CVD in a CVI process to enhance the effectiveness of the infiltration of a matrix material in a fiber preform.

A porous carbon preform has thus been infiltrated by Titanium Carbide TiC at constant temperature (between 850°C and 1050°C) using a pressure pulse of 1 to 5 Torr during 7 sec and 600 Torr during 3 sec. The gas mixture used comprises H2, N2 and TiCl4. However, the depth of the matrix is not more than about 100 µm which remains insufficient for many industrial application.

OBJECTS OF THE INVENTION :

It is an object of the invention to improve the thickness of the infiltrated layer of the matrix material in a preform or the like. Thickness of more than 50 mm can be made.
It is another object of the present invention to provide matrix having an improved density.
It is a further object of the invention to make matrix having a density of at least 95%, with only a few residual closed pores.
It is a further object of the invention to make matrix having a thickness of infiltrated layer of at least 50 mm.

SUMMARY OF THE INVENTION

The invention relates to a process for manufacturing fiber reinforced ceramic material by CVI with simultaneous use of a temperature gradient in the preform and combined pulsed pressure-temperature CVD process, while injecting a mixture of nitrogen hydride and a gas selected from the group comprising silicon hydrides or silicon halides or a mixture thereof.

The use of a cold wall enclosure and asymetrical heating of the sample in said enclosure generates a large thermal gradient through the sample.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a device of CVI according to the prior art processes.
Fig.2 is a device according to the invention wherein the process of the invention can be carried out.
Fig.3 is a schematic drawing illustrating variations of temperature and pressure in the process according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The preform preferably used to carry out the invention is usually made of porous materials having a pore diameter which is preferably between substantially 0.1µm to substantially 100µm. The fibers used to make the preform are continuous, chopped or whisker fibers having a diameter between substantially 1µm to 100µm. THey are made of a large number of materials including SiC, Si_3N_4, C, Al_2O_3, ZrO_2, B, BN, W, Mo, etc... or a mixture thereof.
Whatever the shape of the preform is, the process according to the invention can be applied.
Various gases can be used as a source of gas for silicon nitride matrix deposition according to the invention, such as Silicon Hydrides $Si_n H_{2n+2}$ (preferably SiH_4, Si_2H_6, Si_3H_8,...), Silicon halides (preferably $SiCl_4$, SiF_4, etc...) and Nitrogen hydrides (preferably NH_3, N_2H_4, etc...) or a mixture thereof, bearing in mind that at least two gases are necessary in the CVD enclosure, at least one containing Silicon and at least one containing Nitrogen. Silicon hydrides are preferred to avoid corrosive gas generation at the output of the enclosure.
In order to improve the efficiency of the process according to the invention, it should be in certain circumstances appropriate to remove surface oxide on the fibers used and/or activate the surface of said fibers using a pretreatment in the CVD enclosure or another enclosure prior to Si_3N_4 deposition. This pretreatment is for example made under a reducing atmosphere of H_2, NH_3 or any other appropriate gas, or a mixture thereof.
The apparatus which is preferably used to carry out the process of the invention is disclosed in Fig.2.
Primarily, it comprises infrared heater means 20 such as FORCUS type I.R. heater, placed in the vicinity but outside the LP CVD enclosure 31.
The CVD enclosure 31 is above the I.R. heater 20 which is in front of a SiO_2 glass window of said enclosure which transmits heat into the enclosure 31.
The enclosure itself comprises stainless steel walls 32 with at least a gas imput 26 and at least a gas output 33, a SiO_2 glass plate 22 in front of the SiO_2 glass window 21 supporting a SiC or C plate 23 which, in turn supports the fiber preform 24 with thermocouple means 25 connected to the top and the bottom of said preform 24 for measuring the temperature gradient between the upper and lower surfaces of said preform 24. In order to cool the upper surface of said preform 24 and to maintain and control the thermal gradient in it cooling is provided via a thermally conductive carbon plate 30 in contact with the water cooled stainless steel cover plate 28. The thermocouple means are connected to temperature control means (not represented in fig.2) while gas imput 26 is connected to gas generating means adapted to generate the adequate gas mixture disclosed above and gas ouput 33 is connected to gas pumping means or gas recovery means (not represented in fig.2). The preform 24 is thus submitted to asymetrical heating means, which in the present case is heating means at the bottom and cooling means at the top.
The process will now be explained along with fig.3.
The ceramic or metal fiber preform is introduced into the vacuum chamber, which is first evacuated untill at least 10^{-3} Torr (P1). Then the appropriate gas mixture is injected into the chamber at a pressure P_2 and at a temperature below the decomposition temperature (T1) of said gas mixture. The gases diffuse within the fiber preform quickly. Then, the fiber preform is heated up to the decomposition temperature (T2), generating the deposition of the matrix material from gas phase on to the fibers of the preform.
Then, the reaction chamber is further evacuated down to 10^{-3} Torr and the fiber preform heated up to a temperature (T3) which is higher than T_2. In this last step, the following effects occur :

- Partial crystallization of the deposited matrix materials,
- Improved bonding strength between the deposited matrix layers,
- Opening of closed pores in the deposited matrix materials for the supply of new source gas.
  (This phenomenon occurs by the time the impregnated sample is submitted to the atmosphere pressure, i.e.. when much pressure difference occurs between the outside and the inside of a closed

pore).

- The range of temperature to which the sample is submitted in the enclosure is defined hereunder :

SAMPLE Temperature	T1	T2	T3
Top	RT - 700°C	RT - 700	RT - 1400
Bottom	RT - 700°C	600 - 1400	700 - 1400
T1 = Gas injection temperature in the fiber preform. T2 = deposition temperature. T3 = annealing temperature. RT = Room Temperature			

The relationships between the temperature T1, T2 and T3 are defined as follows :

$30°C < T2 - T1 < T2$
$30°C < T3 - T2 < 1400°C - T2$

The various pressures during the achievement of the process are the following :

	P1	P2
Pressure Range	10^{-5} to 1 Torr	10^{-1} to 10^{3} Torr

Pressures P1 and P2 are linked by the following relationship :

$0.1 \text{ Torr} < P2 - P1 < 10^{3} \text{ Torr}$

The temperature and pressure of the pulsed CVI technique according to the invention comprise three levels of temperature and two levels of pressure in one cycle, as represented in fig.3.
Another important point of the invention is the use of a substantial thermal gradient inside the sample under C.V. infiltration.
The sample is heated from the bottom (here by the FORCUS type IR heater) through two quartz glass plates, 21 and 22 (fig.2).
One (21) is a window of the enclosure and the other (22) is for protection of the gas supply to the bottom of the sample. The quartz glass plate 22 in the enclosure features high melting point, high I.R. transmission and low thermal conductivity. This allows to heat the sample alone up to 1400°C, while the plate 22 remains at a lower temperature.
The top of the sample 24 is cooled by thermal conduction using water circulation within the upper reactor plate through the carbon plate 30 (Fig.2). According to a preferred embodiment of the invention the thermal gradient is preferably equal to at least 20°C/mm and more preferably at least 60°C/mm.
Preferably, the pulse duration (fig.3) might vary between about 5s to about 1 hour.

EXAMPLES :

The following examples have been carried out under the following conditions :
The diameter of the chopped carbon fiber preform used was 40mm, its thickness 5mm and the fibers used were 10μm diameter.
The pulsed injection of Silane SiH_4 and ammonia NH_3 gases were

SiH_4	0.01	liter/pulse
NH_3	0.15	liter/pulse

(these volumes are under Normal pressure and temperature conditions)

- The volume of the enclosure is about 2 liters.

- The pressure P_1 was equal to 10^{-2} Torr while the pressure P_2 was equal to 70 Torr.

The sample Temperatures were the following (fig.3) :

TEMPERATURE	T1	T2	T3
Bottom of sample	400 °C	950 °C	1200 °C
Top of sample	250 °C	300 °C	400 °C

The following pulse pattern has been used (fig.3) :

duration of each pulse : 100s

t1 : 10 s

t2 : 10 s

t3 : 50 s

t4 : 10 s

t5 : 5 s

t6 : 15 s

The pressure hold time Pt_1 (fig.3) which is equal $1/2\ t_1 + t_2 + t_3$ was 65s, and the number of pulses was equal to 1500 (40 hours).

- The following results have been obtained :

Infiltration rate : 1.33µm/pulse

Density of composite : 2.33 g/cm^3 which means about 95% of the theoretical density (2,46g/cm^3) which is the maximum density which could be expected.

- No generation of powder
- Proportion of gas infiltrated as matrix : 25 %

Among the various possible applications of the above invention, one should consider composite manufacturing such as composite manufacturing through deep CVD preform densification, including Fiber Reinforced Ceramics (FRC), Ceramic Matrix Composites (CMC) and Functional Gradient Materials (FGM).

Claims

1. A process for manufacturing fiber reinforced ceramic material by Chemical Vapor Infiltration comprising the steps of introducing a porous preform in a CVD enclosure, evacuating the enclosure at a first pressure (P1), heating up the preform to a first temperature (T1), injecting in said enclosure a mixture of nitrogen hydrides and a gas selected from the group comprising silicon hydrides and silicon halides or a mixture thereof at a flow rate and during a period of time sufficient to reach a second pressure inside said enclosure P2 which is substantially greater than P1, heating up the preform in presence of a substantial thermal gradient accross the preform to at least the decomposition temperature T2 of said gas which is greater than T1, in order to obtain the deposition of a silicon nitride forming matrix material, evacuating the enclosure to said first pressure P1, decreasing the preform temperature to T1, repeating the above steps as long as necessary to obtain infiltration of said preform at the required depth, the first temperature T1 being lower than the decomposition temperature of the gas in said enclosure which is a CVD cold wall type reactor to ensure said substantial thermal gradient accross the said preform.

2. A process according to claim 1 wherein P1 is lower than 1 Torr.

3. A process according to claim 1, wherein P2 is comprised between 10^{-1} Torr and 10^3 Torr.

4. A process according to claim 1, further comprising a step of increasing the temperature of the preform up to the annealing temperature T3 of the matrix material while simultaneously evacuating the enclosure to said pressure P1, then decreasing the preform temperature to T1 and repeating the above steps as long as necessary.

5. A process according to claim 1, wherein T1, T2 and T3 are substantially equal.

6. A process according to claim 1, wherein the relationship between the temperatures T_1 and T_2 is the following :

$30^\circ C < T_2 - T_1 < T_2$

7. A process according to claim 4, wherein the relationship between the temperatures T_2 and T_3 is the following :

$30^\circ C < T_3 - T_2 < 1400^\circ C - T_2$

8. A process according to claim 1 or 4, wherein the ranges of temperatures T_1, T_2 or T_3 are the following :

SAMPLE Temperature	T1	T2	T3
Top	RT - 700°C	RT - 700	RT - 1400
Bottom	RT - 700°C	600 - 1400	700 - 1400

T1 = gas injection temperature in the fiber preform.
T2 = deposition temperature.
T3 = annealing temperature.
RT = room temperature

9. A process according to claim 1, wherein the pressures P_1 and P_2 are according the following relationship :

$0.1 \text{ Torr} < P_2 - P_1 < 10^3 \text{ Torr}$

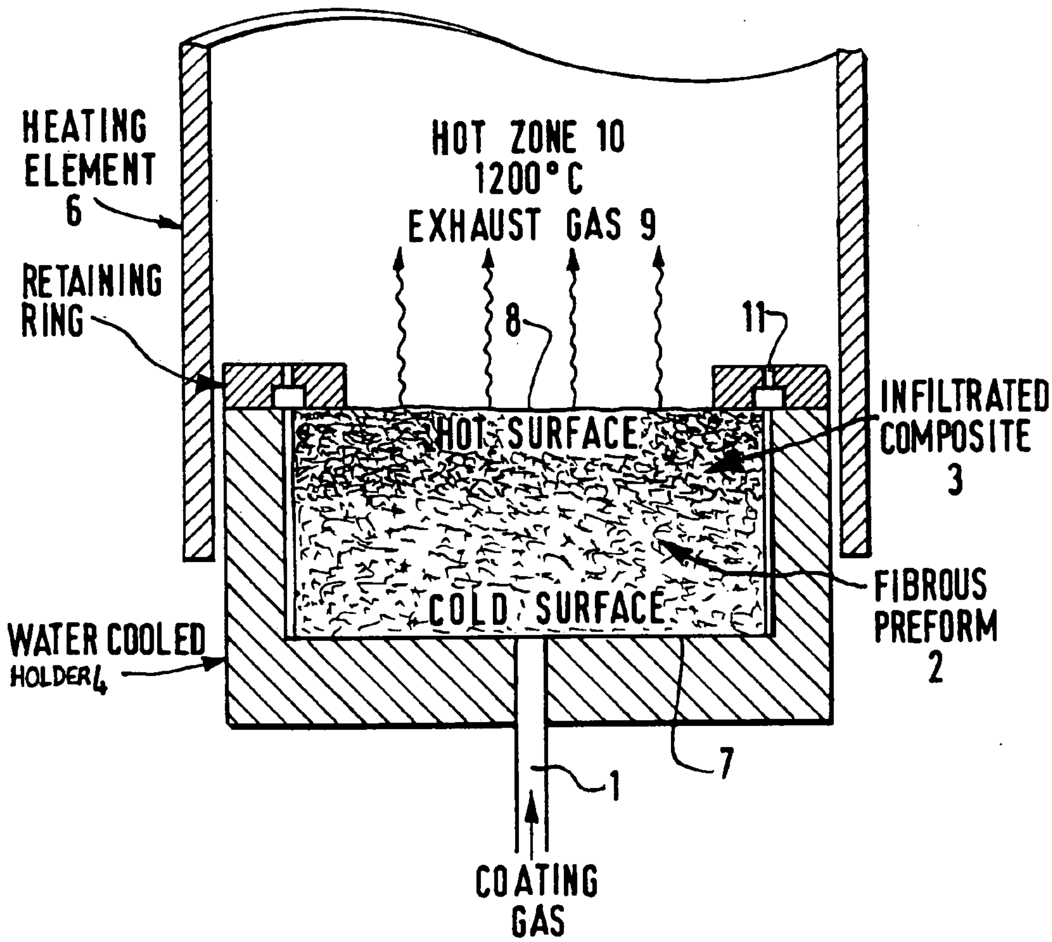
10. A process according to claim 1, wherein the pressures P_1 and P_2 vary within the following ranges :

$10^{-5} \text{ Torr} < P_1 < 1 \text{ Torr}$
$10^{-1} \text{ Torr} < P_2 < 10^3 \text{ Torr}$

11. A process according to claim 1, wherein the thermal gradient in the preform is at least 20°C/mm.

12. A process according to claim 11, wherein the thermal gradient in the preform is at least 60°C/mm.

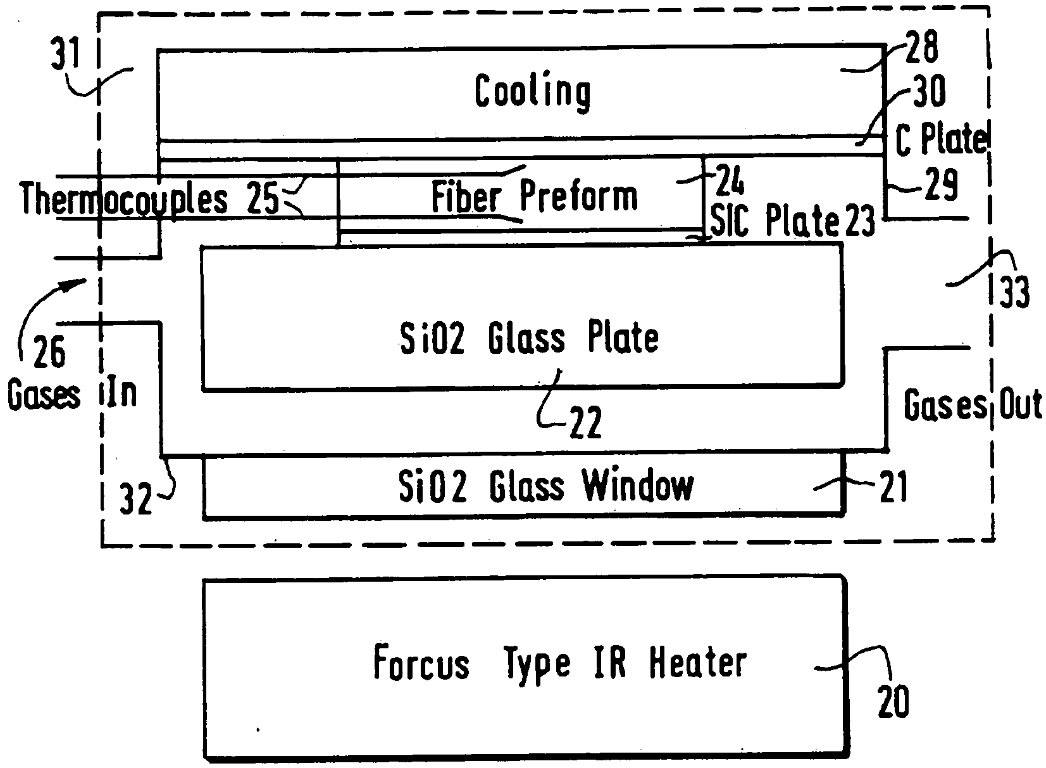
13. A process according to claim 1, wherein the pressure hold time during which the enclosure is under the pressure P_2 is comprised between about 1s to about 1 hour.



ORNL PROCESS

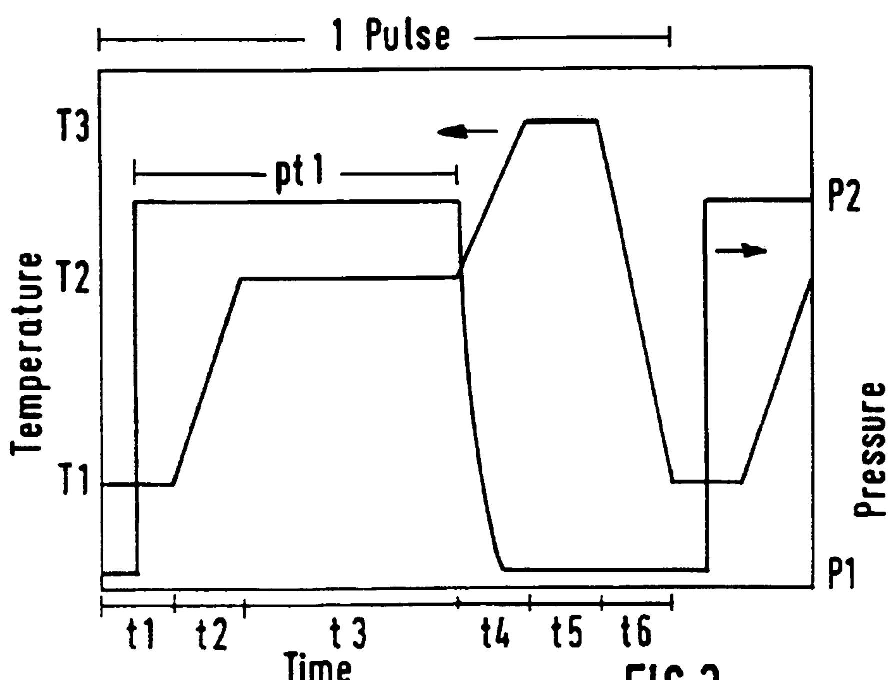
FIG.1

PRIOR ART



31
Cooling
28
30
C Plate
Thermocouples 25
Fiber Preform
24
SiC Plate 23
29
33
SiO2 Glass Plate
26
Gases In
22
Gases Out
32
SiO2 Glass Window
21
Forcus Type IR Heater
20

FIG.2



1 Pulse
T3
pt1
P2
T2
Temperature
Pressure
T1
P1
t1
t2
t3
t4
t5
t6
Time

FIG.3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 40 0405

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
	PROCEEDINGS OF THE ELECTROCHEMICAL SOCIETY vol. 90, no. 12, 1990, pages 546 - 552; T.D.GOLDEN ET AL.: 'FORCED-FLOW THERMAL-GRADIENT CVI OF CERAMIC MATRIX COMPOSITES '		C04B35/80 C01G30/02 C23C16/04 C01G9/02 C04B35/58
X	* the whole document *	1,6,11, 12	
A		1-13	
	US-A-4 895 108 (A.J.CAPUTO ET AL.)		
X	* the whole document *	1	
A		1-13	
A,D	JOURNAL OF MATERIAL SCIENCE LETTERS vol. 6, 1987, pages 331 - 333; K.SUGIYAMA ET AL.: 'PULSE CVI OF POROUS CARBON ' * the whole document *	1,3,13	
X	US-A-4 980 202 (J.J.BRENNAN ET AL.) * the whole document *	1,3,11, 12	
A	US-A-4 580 524 (W.J.LACKEY ET AL.)		
A	WO-A-8 704 733 (SOCIETE EUROPEENNE DE PROPULSION)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C04B
C01G
C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 SEPTEMBER 1991	HARBRON J.L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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